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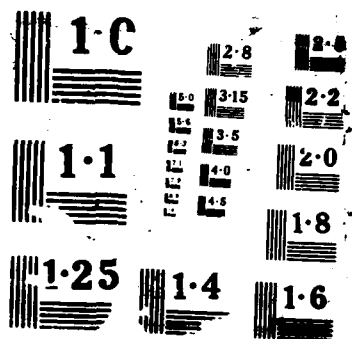
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An Investigation of the Crystalchemistry and Thermochemistry
Of Selected Mineral Systems

Robert R. Reeber
Department of Geology
Mitchell Hall 029A
University of North Carolina-CH
Chapel Hill, N.C. 27514

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ABSTRACT

A computer-controlled travelling Laue x-ray camera and small rapid response furnace system was designed, constructed and operated for the study of phase transitions in solid state systems. The camera is capable of continuously monitoring crystallographic phase changes occurring in small single crystal samples over a temperature range from 100 to 1000K. Extensive studies of complex structural changes in natural crystals of tridymite were completed. Some preliminary experiments were also made with single crystals of CdS and CdTe. All materials were characterized with transmission electron microscopy. Defect and strain distributions in CdS and CdTe crystals were also examined with synchrotron white beam topography. This report gives a brief overview of results accomplished. It includes a list of papers and abstracts published during the course of the research.

INTRODUCTION

Phase transition behavior in the solid state is often complicated and constrained. A phase transition is essentially a means for a particular configuration of vibrating atoms to reduce energy through rearrangement into a new dynamic configuration with a lower energy content. The configuration observed at a particular time under specific environmental conditions is the result of the ability of an earlier configuration to find a energy dissipative transition path or paths. Because of the many complexities that can arise for such behavior it is useful to continuously observe the crystallography of single crystal samples as a function of changing environmental variables. Material and mineral properties are a strong function of the structural state as well as defect types and distributions of the substance in question. Mechanical, electrical, magnetic, optical, thermal and chemical properties are all affected to varying degrees by specific processing steps which change structure and/or defects. Often many trial experiments must be carried out before optimum processing conditions are obtained that provide a desired product. Although thermal methods such as differential thermal analysis and scanning calorimetry are helpful they often are not sensitive enough to see or separate out important aspects of phase transition phenomena.

In the earth sciences, for systems where remnant structures are a function of the thermal/pressure path, structure and defects often can give clues to help in unraveling geological history.

RESEARCH PROJECT RESULTS

1. One of the principal aspects of this work was to design, build and operate a computer-controlled x-ray camera that could directly observe and continuously record the effect of changing environmental conditions on the structure of solids. An important aspect of the approach was to be able to provide some information on the kinetics of phase changes. Figures 1 and 2 give respectively, schematics for the traveling Laue camera (TLC) and associated computer controls. The camera is based upon an earlier prototype (Reeber 1975). It combines the simplicity of the Laue method and a low-mass-quick-response minifurnace with a moving film plate to record phase transitions in minerals and other materials. Plate 1 illustrates a typical x-ray film of complex phase changes in the structure of natural crystals of tridymite. More complete details on the TLC and its computer control program will be published elsewhere (Smelik 1987 and Reeber et al 1988).

2. As has been indicated earlier phase transition behavior for some ceramic and mineral systems is complex and often kinetically hindered. The structure at a particular temperature and pressure is in many cases constrained by the absence of viable energy dissipative paths to equilibrium. These may or may not be time dependent. Where initial structures are complex, as for instance tridymite, the corresponding diffraction record is also complex and difficult to determine quantitatively. As a first step in this process we have developed a concept called the thermal diffractogram (TD). This is simply a histogram plot of the number of changing diffraction spots as a function of temperature. The TD illustrated in Figure 3 qualitatively illustrates the degree of structural change occurring in a tridymite crystal from Topaz Mountain, Utah. The amount of detail observable is significantly more than can be obtained from thermal measurements such as DTA. Further details are given in a Master's thesis accomplished as part of this research (Smelik 1987) and will be published elsewhere. A review paper on Phase Transformations was published (Reeber 1983a).

3. The Army has a large program through MICOM addressing growth of CdS crystals for Ultraviolet sensors. Part of this project was aimed at finding better ways to characterize such crystals and to understand the interrelationships between their optical properties and structure. Synchrotron topography, high resolution electron microscopy as well as a limited amount of TLC x-ray experiments were carried out with both high and low resistivity crystals grown by vapor transport. Crystals were supplied by MICOM, General Dynamics and Eagle Picher Corporation. The Brookhaven National Light Source was utilized for the white beam topography experiments. Preliminary results for this work was presented in the spring of 1987 at a MICOM Workshop on Sensors for Smart Munitions. A paper was submitted for the Workshop Proceedings. The results indicate that the synchrotron is a useful tool for evaluating defect and strain distributions in compound semiconductors and can provide useful information to the crystal grower that is necessary for crystal quality improvement. White beam topography is especially useful when used in conjunction with high resolution electron microscopy. The latter method is able to identify specific defects responsible for strain effects observed by topography.

4. Although the scope of this work was to develop experimental methods for studying phase transitions some effort necessarily was expended to interpret the results obtained. In addition to the computer program designed to control our experiments several programs were written to aid in indexing the crystallographic data obtained. These included programs to calculate interplanar angles for different crystallographic symmetries as well as to calculate experimental interplanar angles from measured information on our x-ray films were written. The logic has been developed to extend these programs so that eventually each x-ray film can be automatically indexed. It is hoped that such information can eventually supply input for additional graphics programs which when written will clearly illustrate crystallographic cell distortions as a function of changing environment.

5. The original work plan included building equipment to measure low temperature thermal expansion with capacitance dilatometry. This had been planned for the third year. Early in the project an opportunity became available to complement the x-ray work more directly with then currently inactive electron microscopy facilities in the UNC-CH Physics Department. Since this was more compatible with the phase transition work the scope was changed and the TEM facilities were repaired and upgraded. An ion mill was constructed for sample preparation and more extensive experiments were carried out for tridymite, CdS and CdTe. Higher resolution work was done in conjunction with the Institute of Electron Microscopy, Fritz Haber Institute, Berlin. A theoretical paper was published early in the project relating brittle-ductile transition temperatures to lattice vibrational properties (Reeber 1983b). Although the experimental thermal expansion work was not carried out as originally planned a critical review paper was published on the thermal expansion of II-VI and II-V compound semiconductors (Reeber & Haas 1985).

DEGREES GRANTED:

Mr. Eugene Smelik successfully defended his master's thesis in November of 1987 and will graduate in December 1987. He is currently continuing his graduate studies at the Johns Hopkins University in Baltimore.

PUBLICATIONS:

1. Reeber, R.R. (1983a) "Phase Transformations at Low Temperatures", Chapter 12, pp254-256. Crystallography in North America Editors D. McLachlan Jr. and J. Glusker American Crystallographic Association.
2. Reeber, R.R. (1983b) "Corresponding States Aspects of the Brittle to Ductile Transition in Diamond and Sphalerite-Structure Solids, Fracture Mechanics of Ceramics 6: pp545-554, edited by R.C. Bradt, A.G. Evans, D.P.H. Hasselman and F.F. Lange Plenum Press, N.Y.
3. Reeber, R.R. and Haas, J. (1985) "Thermal Expansion of Ten Grimm-Sommerfeld Compounds" Thermal Expansion 8 Editor, Thomas A. Hahn pp31-48, Plenum Press, N.Y.
4. Reeber, R.R. and Smelik, E. (1986) "X-ray Technique for Continuous Observation of Phase Transformations", Journal of Metals Abstract April 1986.
5. Reeber, R.R. and Tesche, B. (1987) "Synchrotron Topography and Electron Microscopic Characterization of II-VI Semiconductor Crystals", Proceedings of the MICOM Workshop on Electronic and Electrooptical Materials for Smart Munitions 13-14 May 1987 in press.
6. Smelik, E. and Reeber R.R. (1987) "Kinetics and Crystallography of Tridymite Transitions", Abstract American Geophysical Society Meeting Baltimore, Md. May 1987.
7. Smelik, E. A., (1987) "An X-ray Diffraction Study of Displacive Phase Transitions in Terrestrial Tridymite", Master's Thesis University of North Carolina-CH, December 1987.

Several additional publications are in preparation.

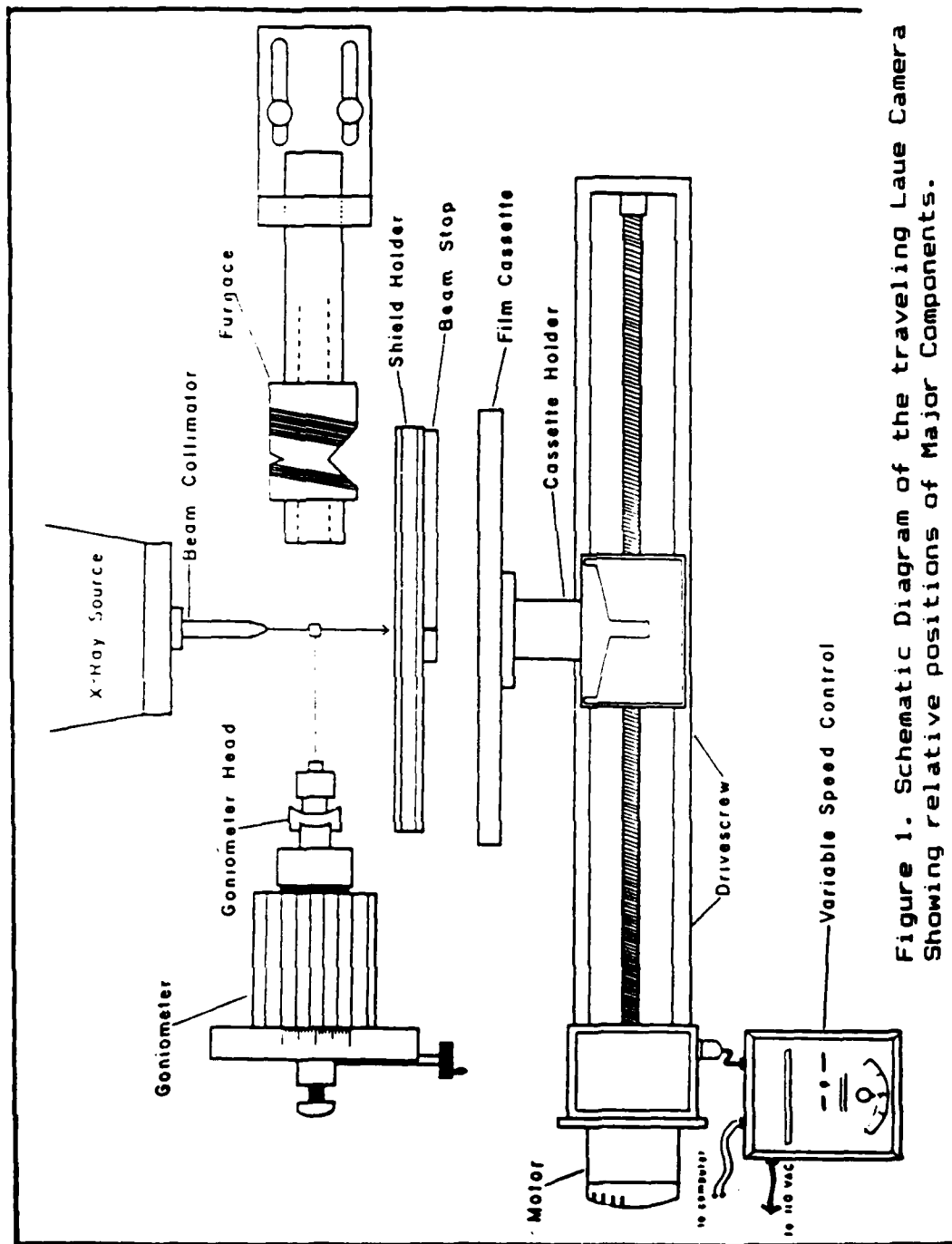


Figure 1. Schematic Diagram of the traveling Laue Camera Showing relative positions of Major Components.

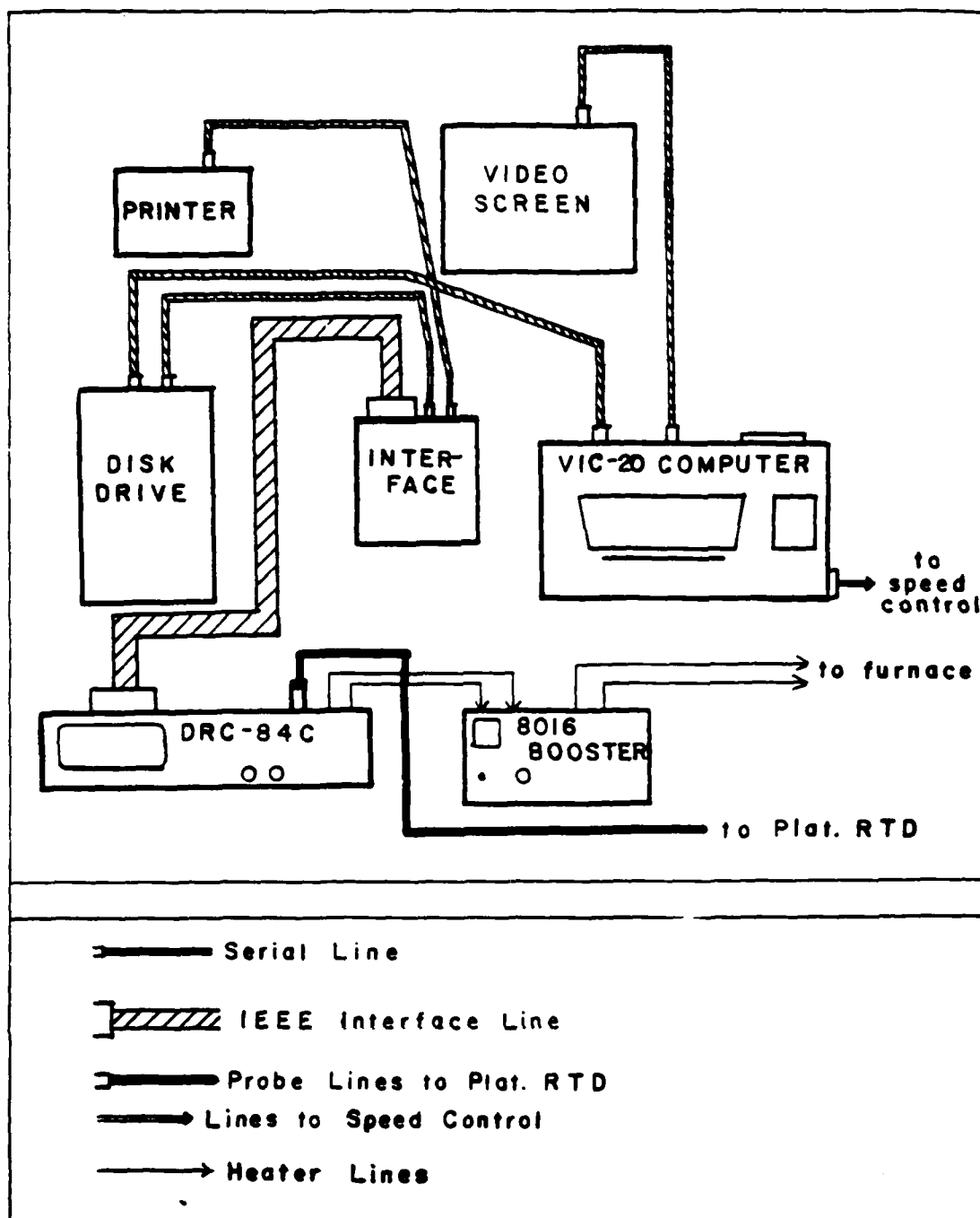


Figure 2. Schematic of Computer Control System for the Traveling Laue Camera (TLC).



PLATE 1. Typical Traveling Laue Film for a Tridymite Crystal, Run 97T. Note major transformation that occurs at about 160 C.

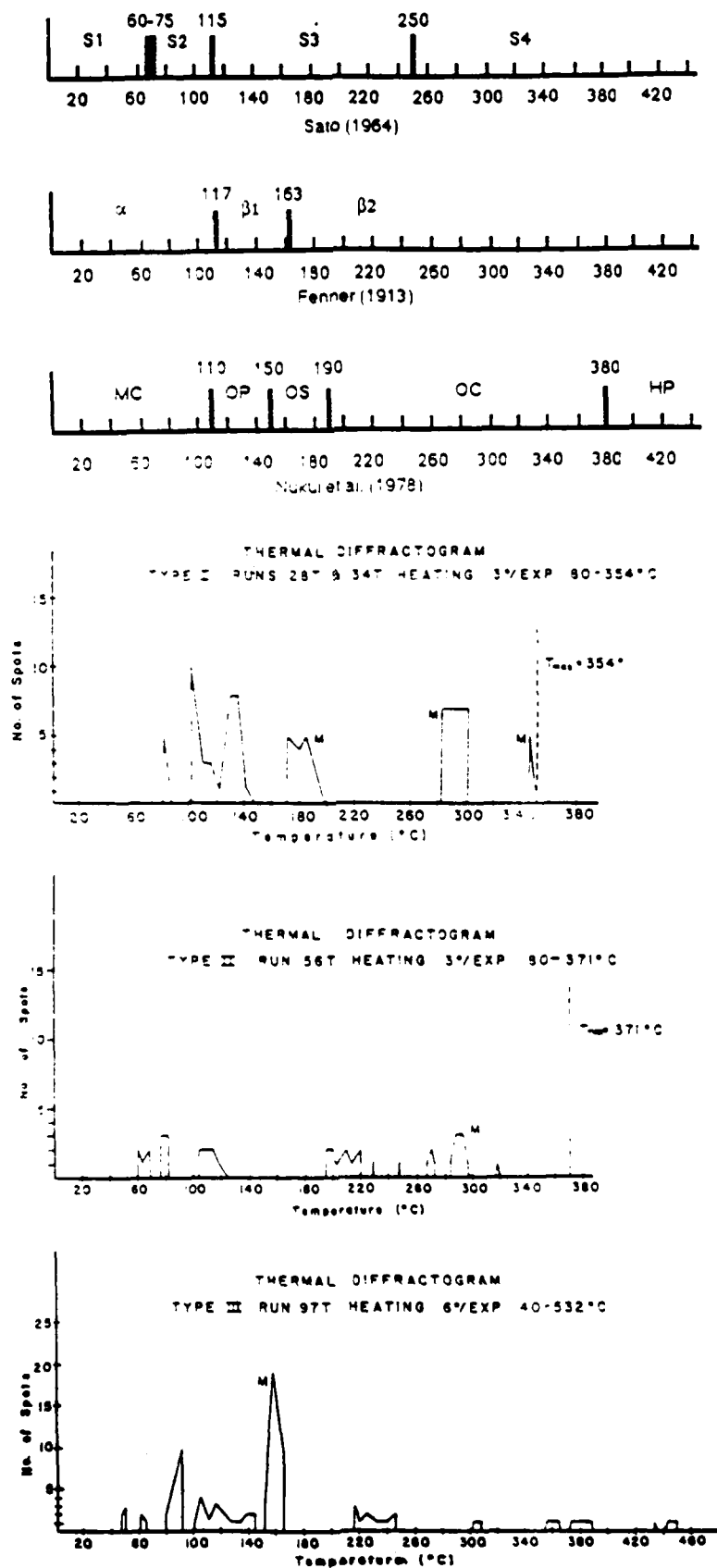


Figure 3. Summary of Phase Transformation Behavior of Three Types of Tridymite Crystals. Thermal Diffractograms are shown for each type of behavior along with three transformation schemes from the literature. Note that although the published transformation schemes can be picked out on the thermal diffractograms, the traveling Laue Method reveals much additional information.

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